POLYARYLENE-ALKYLENE SULFIDES

BY

PHILIP DORNIN CAESAR

B.S., Yale University, 1939
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

The reaction between thiol groups and carbon-carbon double bonds to produce linear polymers of high molecular weight is not new.[1,2] However, at the time of this work such reactions were limited to the copolymerization of aliphatic dithiols and aliphatic, non-conjugate diolefins; in particular, to the copolymerization of hexamethylenedithiol and biallyl. Therefore, a primary objective of this investigation was the preparation of linear high molecular weight polymers by the reaction of dithiols and diolefins, either or both containing an aryl nucleus. Of special interest was the extension of this reaction to include dithiols in which the thiol groups were attached to the aryl nucleus.

Discussion

High molecular weight linear polymers have been prepared by emulsion polymerization of aryl dithiols with biallyl. The melting point of dithiol-diolefin copolymers has been raised from the maximum of 86° for polyalkylene sulfides[1] to 225-235° for the polyarylene-alkylene sulfide prepared from biphenyl-4,4′-dithiol and biallyl. Such polymers were found to be very insoluble in organic solvents.

Emulsion polymerization using peroxide initiators with and without reduction activation has been the most successful means of obtaining these polymers. An initiator system consisting of ammonium peroxydisulfate, sodium hydrogen sulfite and copper(II) sulfate[3] was used at 30° with the emulsifier, MP189-EF, buffered with sodium acetate and adjusted to a *p*H of 3.35.[4] It was found that a small amount of benzene or methanol in the system gave better yields of high molecular weight polymers, and that reaction temperatures of 50° and higher were necessary for the formation of those polymers that melted above 150°. At polymerization

temperatures of 50° and above, no sodium hydrogen sulfite could be tolerated in the system.

Two methods for the preparation of aryl dithiols have been utilized. The first was the reduction of aryl sulfonyl chlorides with zinc dust and acid. It was found that more reproducible results could be obtained by amalgamation of the zinc dust prior to its use as a reducing agent. This process seemed to be limited, however, to those aryl disulfonyl chlorides that gave reduction products of relatively low melting point and high solubility. For the preparation of the dithiols of higher melting point, it was necessary to use a second, less familiar reduction technique. The aryl disulfonyl chloride was reduced at 80° by a solution of tin(II) chloride 2-hydrate dissolved in glacial acetic acid saturated with hydrogen chloride.[5]

The high degree of purification of the aryl dithiols requisite for polymerization has been realized by using the following steps. The first involved the purification of the original aryl disulfonyl chloride to eliminate those impurities which might reduce to thiols with properties similar to those of the desired product. The second step was the sublimation of the dithiol in a molecular still under high vacuum. The third and final step was to dissolve the dithiol sublimate in a dilute alkaline solution and to reprecipitate the dithiol immediately by filtering the alkaline solution into excess acid.

Investigation of the higher molecular weight polymers from aromatic dithiols and biallyl prepared by emulsion polymerization has shown that orientable fibers could be drawn from a hot melt of the polymer. It was found possible to orient fibers from a polymer with an inherent viscosity above 0.4. The strength of the fiber, however, seemed to be as much a function of the configuration of the molecule as of the molecular weight. For example, two polymers prepared from diphenylmethane-4,4′-dithiol and phenoxybenzene-4,4′-dithiol with the same melting point and inherent viscosity gave very strong and very weak fibers, respectively. X-ray patterns made by Mr. J. Fuchs showed that the stretched fibers were oriented.

The following polyarylene-alkylene sulfides were prepared.

Repeating Unit	Melting Point
[(p) S-(C_6H_4)-CH_2-(C_6H_4)-S-(CH_2)$_6$]	120-121°
[(p) S-(C_6H_4)-O-(C_6H_4)-S-(CH_2)$_6$]	118-119
[(p) S-(C_6H_4)-(C_6H_4)-S-(CH_2)$_6$]	225-235
[(p) S-(C_6H_4)-S-(CH_2)$_6$]	155-159
[(1,5) S-($C_{10}H_6$)-S-(CH_2)$_6$]	148-151
[(2,6) S-($C_{10}H_6$)-S-(CH_2)$_6$]	> 183
[(2,7) S-($C_{10}H_6$)-S-(CH_2)$_6$]	——

Lithium aluminum hydride has been used to reduce alkyl and aryl sulfonyl chlorides to the corresponding thiols, and aryl sulfones to aryl sulfinic acids. Aryl sulfonamides and esters of aryl sulfonic acids were not reduced in this manner.

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VITA

The author was born in New Haven, Connecticut, on March 13, 1917. He attended the public schools of Tacoma, Washington for all but his high school senior year. He graduated from the Taft Preparatory School in Watertown, Connecticut, in June, 1935. In September of that year he entered Yale University, from which he received the degree of Bachelor of Science in June, 1939. From July, 1939, to the present he has been employed as a chemist by the Socony-Vacuum Oil Co., Inc. In April, 1940, he was married and subsequently had two children. In September, 1947, he was sent on a company scholarship to the graduate school of the University of Illinois.

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